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Friction and wear of carbon nanohorn-containing polyimide composites

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Polyimide (PI)-based composites containing single-wall carbon nanohorn aggregate (NH) were fabricated using the spark plasma sintering (SPS) process. For comparison, composites with carbon nanotube (NT) and traditional graphite (Gr) were also fabricated. The NH was produced using CO_2 laser vaporization and a graphite target and the NT was produced by a chemical synthesis method. We evaluated the friction and wear properties of the PI-based composites with a reciprocating friction tester in air using an AISI 304 mating ball. NH drastically decreased the wear of PI-based composites; the specific wear rate of composite with NH of only 5 wt% was of the order of 10^{-8} mm^3/Nm, which was two orders of magnitude less than that of PI alone. The wear reduction ability of NT seemed to be slightly inferior to that of NH, although it was considerably better than that of Gr. NH and NT lowered the friction of composites. The friction coefficient of composite with 10 wt% NH was less than 0.25, although it was slightly higher than that of composite with 10 wt% Gr. There was no clear difference in the friction reduction effect of NH and NT. The further addition of Gr to composites with NH or NT rather deteriorated the antiwear property of composites, although the friction coefficient was slightly reduced. The transferred materials existed on the friction surface of the mating ball, sliding against composites with three types of carbon filler. These transferred materials seemed to correlate with the low friction and wear properties of composites.

KEY WORDS: carbon nanohorn, carbon nanotube, graphite, polyimide, composite, friction, wear

1. Introduction

The discovery of carbon nanotubes [1] has attracted widespread interest and many studies on mass production, evaluations, and applications have been conducted. Recently, a single-wall carbon nanohorn (SWNH), part of the carbon nanotube family, was produced by CO_2 laser vaporization of graphite at room temperature [2,3]. The individual SWNH is a horn-shaped sheath composed of single-wall graphene sheet, 2–4 nm in diameter and about 50 nm long. The SWNH always aggregates to form a spherical particle with multiple horns; the average diameter is 80–100 nm.

The SWNH aggregate (NH) has good properties such as high adsorption, easy chemical modification, and high electric conductivity. Its high adsorption is especially attractive for fuel cell technology. Besides those properties, the NH is expected to display good tribological properties, because of its spherical shape with sub-micron diameter. However, the tribological properties of NH have scarcely been studied, even though those of carbon nanotubes have been considerably determined [4–14]. We have therefore been investigating the tribological properties of NH as an additive in grease and polymer-based composites.

In this paper, the friction and wear properties of NH-containing polyimide composites are reported and compared with those of composites with carbon nanotube and graphite. The tested composites were fabricated by the spark plasma sintering (SPS) process; their friction and wear properties were evaluated using a reciprocating friction tester in air.

2. Experimental

2.1. Composites

NH was produced using CO_2 laser vaporization and a graphite target as detailed elsewhere [2,3]. Ar was used as the buffer gas and was filled in a reaction chamber to a gas pressure of 0.1 MPa. TEM and SEM images of NH are shown in figure 1. The average NH had a diameter of 80–100 nm. As a carbon nanotube, multiwall carbon nanotubes (NT) produced by a chemical synthesis method using hydrocarbon and ultrafine catalyst particles were used [15]; they were 10–50 nm in diameter and several μm long (figure 1). The graphite used was commercially available graphite powder with

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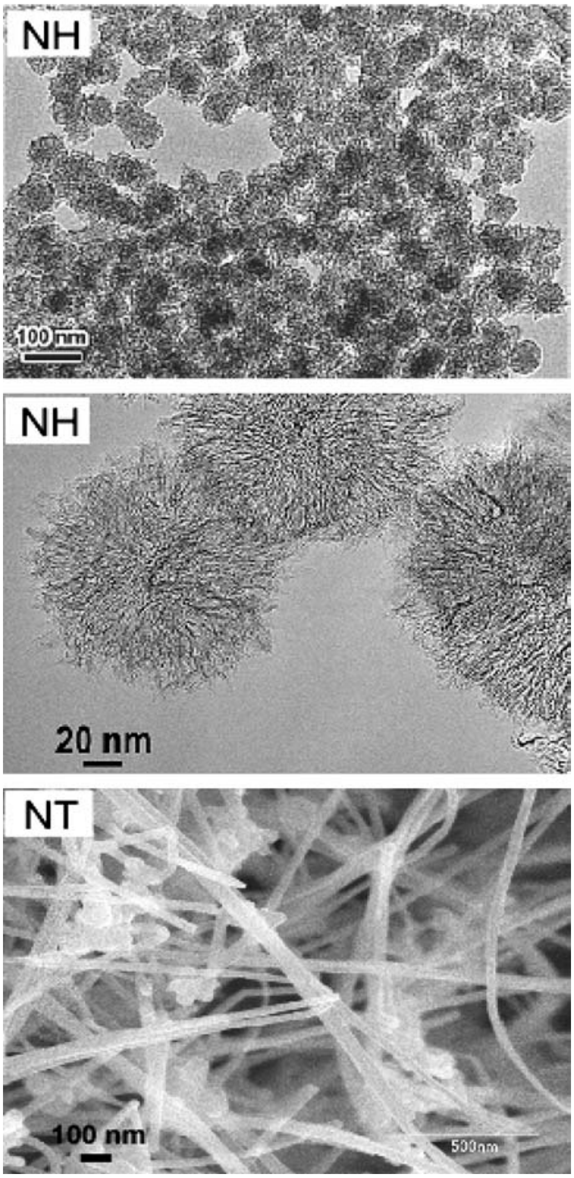

Figure 1. Micrographs of single-wall carbon nanohorn aggregate (NH) and multi-wall carbon nanotube (NT).

an average size of 0.6 μm, T-1 (Nippon Graphite Industries, Ltd.). Polyimide (PI) used as a base material was Kerimid 1010 (Nippon Polyimide Co.) with a powder size of less than about 50 μm.

PI-based composites were made using the SPS process. This process is a pressure sintering process utilizing on–off DC pulse energizing (figure 2), as detailed elsewhere [16,17]. The PI powders and carbon fillers were blended with a stirrer in ethanol and then dried. Blended powders were laid as the carbon-containing surface layer on PI substrate powders in a graphite mold of SPS. The composite was then sintered at a pressure of 50 MPa and a temperature of 220 °C, which was monitored by a thermocouple inserted into the mold, for 5 min. Some composites were sintered at higher temperatures such as

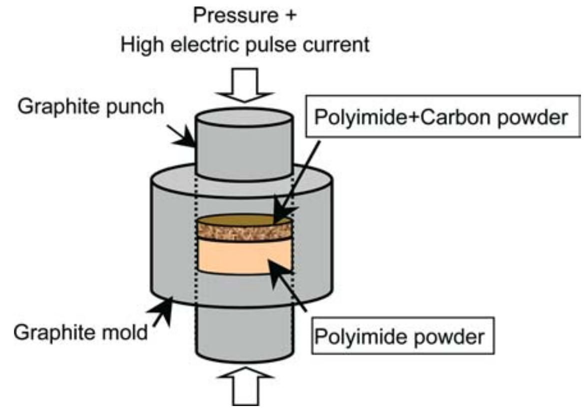

Figure 2. Main part of spark plasma sintering process.

250 and 280 °C, but cracks were found in the sintered composites and their antiwear properties were worse. Composites were 20 mm in diameter and 6-mm thick, with a 1-mm thick carbon-containing surface layer. The surfaces of composites were ground by emery paper of different abrasive particle sizes, and then polished with alumina slurry (powder size: <2 μm). The average surface roughness Ra of polished composites ranged from 0.02 to 0.05 μm; the roughness seemed to increase with higher carbon filler content.

The polished composite surfaces observed using an optical microscope are shown in figure 3. The carbon fillers dispersed in the boundaries of PI powders, although some filler cohesion was seen. The Vickers hardness of some composites was measured at a load of 0.49 N (figure 4). The hardness of composites with 10 wt% NH and 10 wt% NT was significantly higher than that of PI alone; the composite with NT seemed to be slightly harder than the NH-containing composite. The hardness of composite with 10 wt% Gr, on the other hand, was a little lower than that of PI alone.

2.2. Friction tests

Friction and wear tests were done using a ball-on-block type reciprocating friction tester. The mating was an austenitic stainless steel (AISI 304, H_v = 2.7 GPa) ball of 9.2 mm diameter. The reciprocating friction stroke was 10 mm and tests were conducted at normal loads of 5 and 25 N. Average sliding speed was 20 mm/s (60 cycle/min) and the number of cycles was 7200. The test environment and temperature were ambient air and room temperature, respectively. During the tests, the friction coefficient was continuously measured using a load cell. The wear volume of the composite was calculated by measuring wear scars with a non-contact type surface profilometer. Two tests were conducted to examine the scatter of friction coefficient and wear rate, except for some cases.

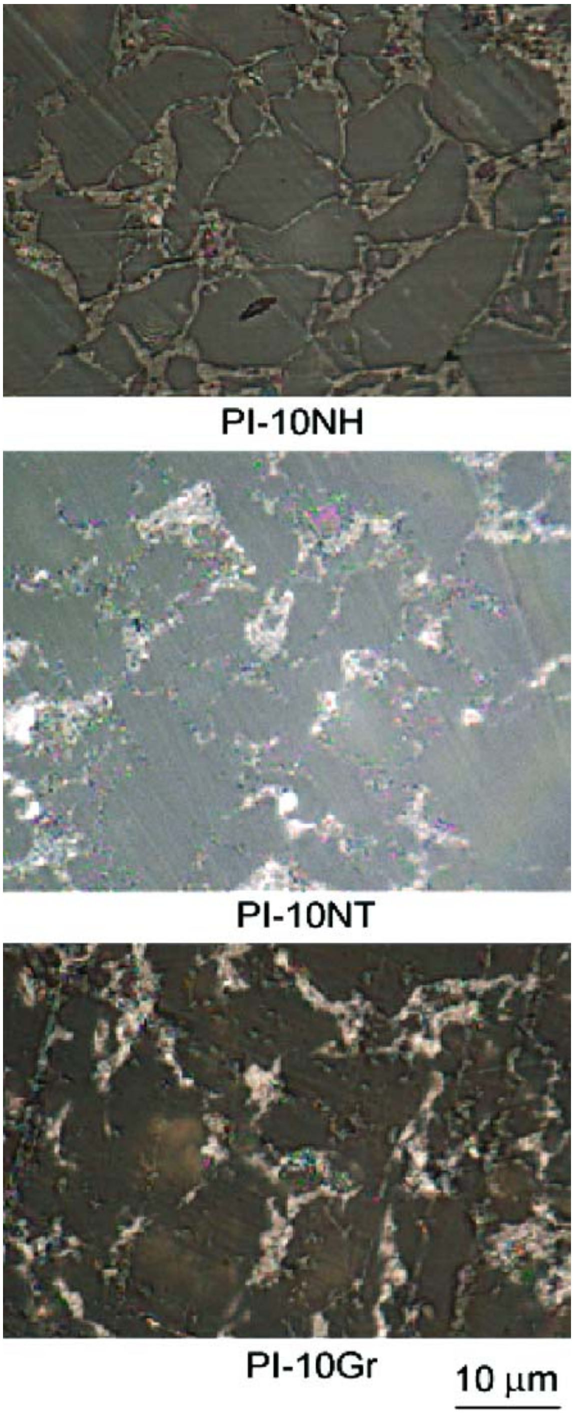

Figure 3. Surfaces of composites with NH, NT, and Gr of 10 wt%.

3. Results and discussion

3.1. Friction behavior

The friction behavior of PI alone and composites with three types of carbon filler of 10 wt% is shown in figure 5. For PI alone, the friction coefficient increased during early testing, and then reached a steady value, regardless of the normal load. The friction coefficient of composites with three types of carbon filler increased during the very early stage, then decreased gradually, and finally approached a steady value, irrespective of the load. Another composite with different carbon content showed similar friction behavior to those of the composites shown in figure 5. The friction coefficient of composites shown in later figures is the average value in the steady state.

3.2. Effect of carbon content and type on friction and wear

The relationship between friction of composites with three types of carbon filler and filler content is shown in figure 6. With Gr-containing composite, only composite with 10 wt% Gr was manufactured, as many studied suggested that the addition of 10% Gr sufficiently lowered the friction and wear of composites [18–20]. The vertical bars in figure 6 show the scatter range of two tests. When NH was added to PI, the friction coefficient clearly decreased; the friction decreased with increasing NH content up to the content of 10%, irrespective of the normal load. The friction difference between the composite with 10% NH and that with 50% NH was very small. The relationship between friction of composites with NT and content was similar to that of NH-containing composites. There was no clear difference in friction reduction effect between NH and NT: the friction coefficient of composite with 10% NH was almost the same as that of composite with 10% NT. The friction of composite with 10% NH seemed to be slightly higher than that of composite with 10% Gr.

Figure 7 shows the relationship between specific wear rate of composites with three types of carbon filler and content. When 5% of NH was added, the specific wear rate of composite was drastically reduced, regardless of the normal load. For composites containing 10 or 50% NH, the wear rate increased; especially, the wear rate of the composite with 50% NH was about 10 times that of the composite with 5% NH. The dependency of wear on NH content was different from that of friction shown in figure 6. This disagreement must be caused by that the excessive addition of NH to composite deteriorated its mechanical strength, although the friction maintained a low value. The addition of NT clearly reduced the specific wear rate of composites, although there seemed to be no clear difference in the wear rate between composites with 5% NT and 10% NT. The wear reduction ability of NH was slightly better than that of NT; the composite containing 5% NH had a very small wear rate of less than 5×10^{-8} mm^3/Nm. The composite with 10% Gr showed a much higher wear rate than those with NH or NT.

3.3. Effect of carbon compound addition on friction and wear

Figure 6 showed that Gr is more effective to lower the friction of composites, compared with NH or NT. So,

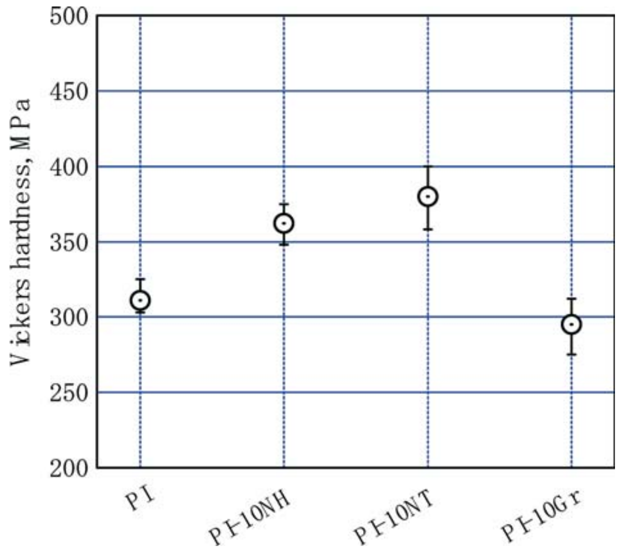

Figure 4. Vickers hardness of composites.

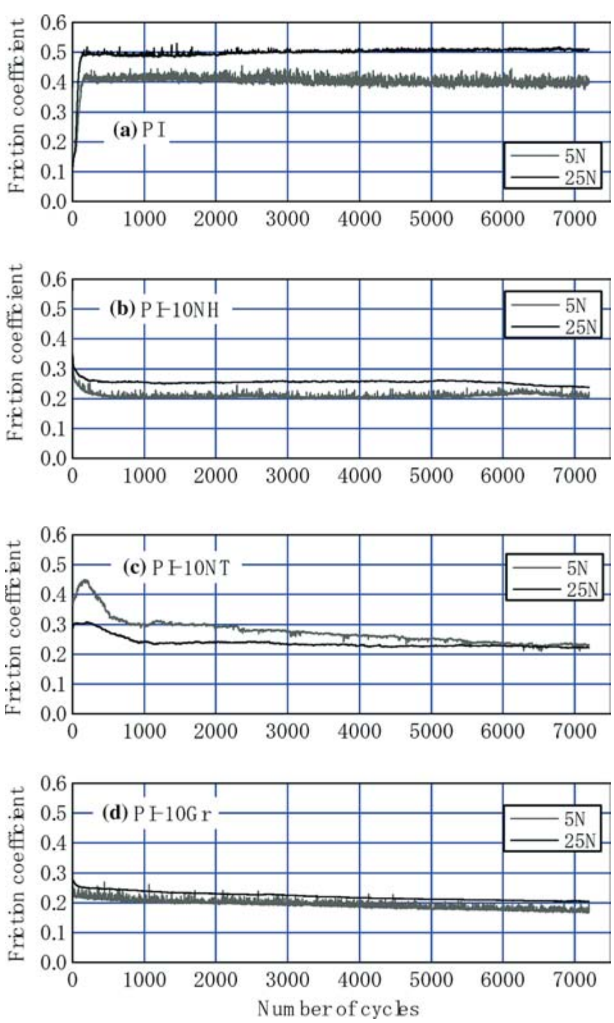

Figure 5. Friction behavior of composites with different carbon fillers.

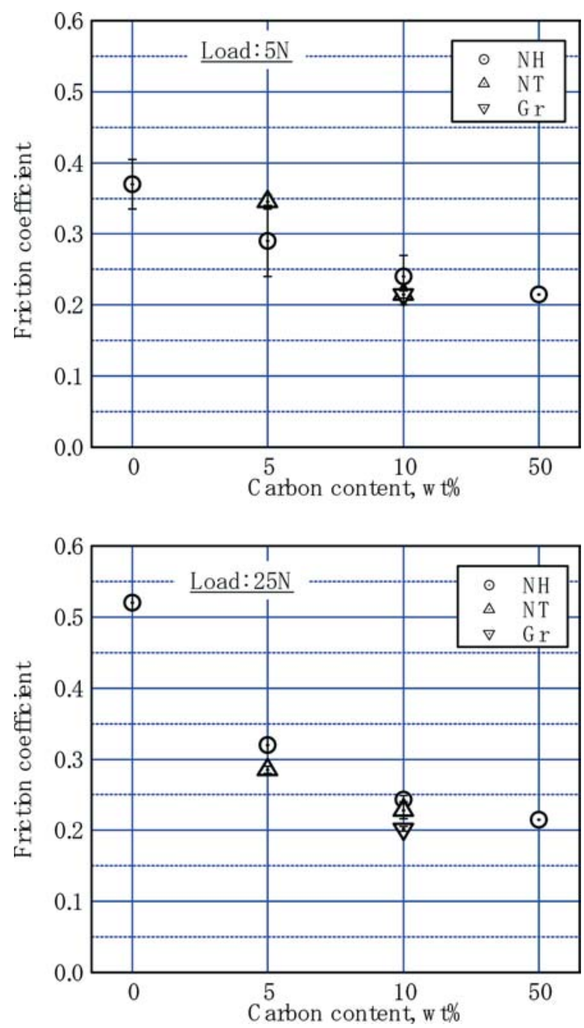

Figure 6. Friction coefficient of composites versus carbon filler content.

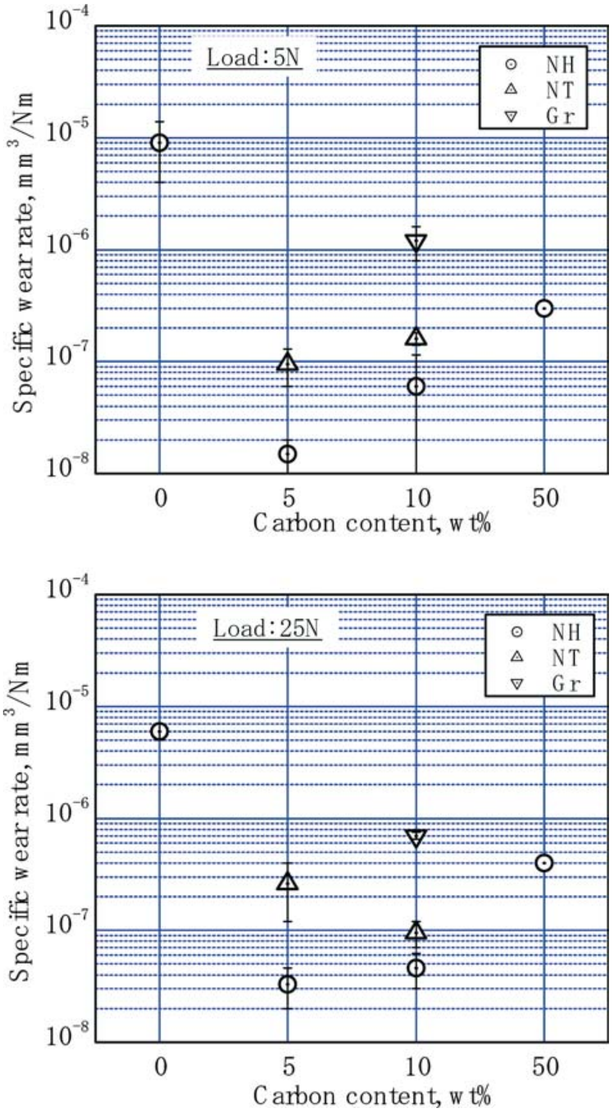

Figure 7. Specific wear rate of composites versus carbon filler content.

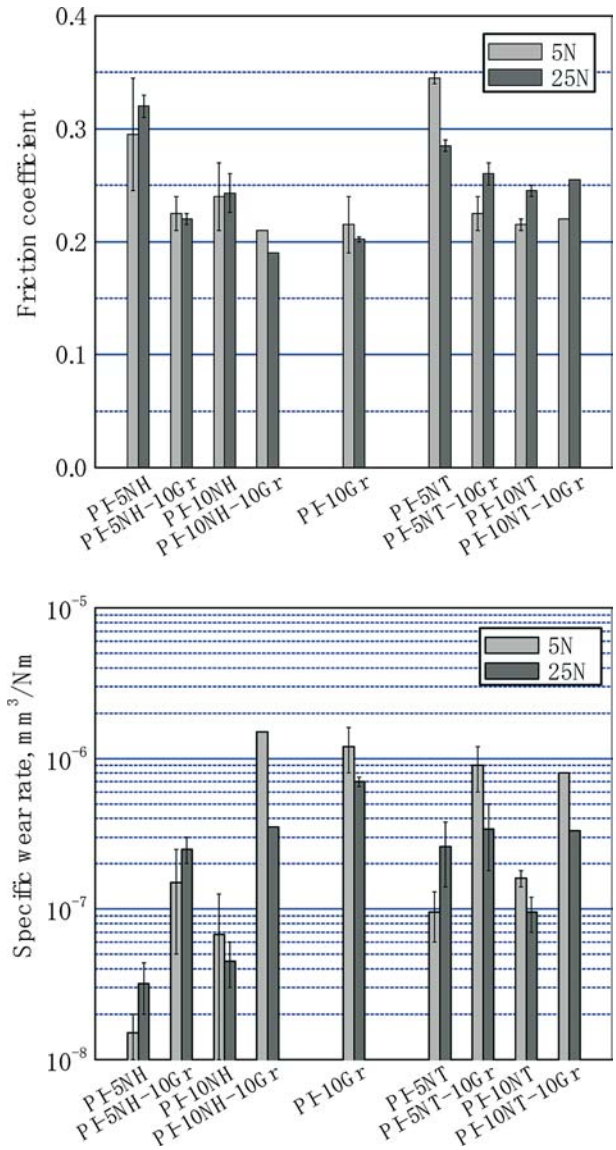

Figure 8. Friction and wear of composites with both Gr and NH or NT.

composites containing with both 10% Gr and 5–10% NH or NT were manufactured. Their friction and wear properties are shown in figure 8. The friction coefficient of composites with both Gr and 5 or 10% NH was obviously lower than that with NH alone; the former composites had almost the same friction as the composite with Gr alone. On the contrary, the specific wear rate of composites with both Gr and NH remarkably increased compared with that of composites with NH alone. For the compound addition of Gr and NT, the friction coefficient of composite with both Gr and 5% NT was lower than that of composite with NT alone, although there was no clear difference in friction between the composite with both Gr and 10% NT and that with NT alone. The wear of composites containing both Gr and 5 or 10% NT clearly increased compared with that of composite with NT alone. These results show that the further addition of Gr to composites with NH or NT deteriorates their antiwear property, although the friction coefficient is reduced.

Figure 9 shows the friction surface profiles of mating AIST 304 balls, which were measured with a non-contact type surface profilometer. We could not find any worn part around the top of the balls, suggesting that the mating balls suffered negligible wear. Therefore, with other composites and test conditions, the ball wear could be disregarded.

3.4. *Friction surfaces*

Friction surfaces on the composite were observed by optical microscopy and SEM. Figure 10 shows the friction surfaces on the composites with 10% carbon fillers and PI alone. For PI alone, the friction surface

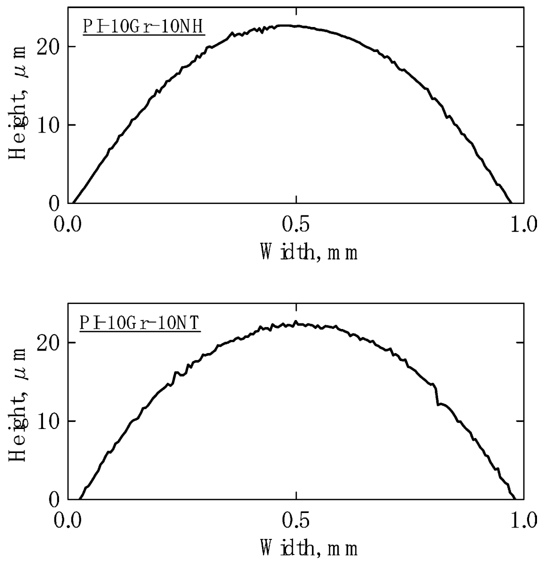

Figure 9. Friction surface profiles of mating AISI 304 balls sliding against PI-10NH-10Gr and PI-10NT-10Gr at a load of 25 N.

was considerably roughened and there were many large vertical cracks in the direction of friction. The friction surfaces on PI-10NH and PI-10Gr, on the other hand, were generally smooth, although some scratched lines were seen. For PI-10NT, there were many scratched lines on the friction surface compared with the composites with NH or Gr. Figure 11 shows high-magnification SEM micrographs of the friction surfaces on the composites with 10% carbon filler. With PI-10NH and PI-10NT, small thin cracks were seen on the friction surfaces, whereas large cracks existed here and there on the friction surface of PI-10Gr.

Figure 12 is an optical micrograph of the friction surfaces on mating AISI 304 balls. For PI alone, the friction surface of the ball seemed to be scarcely covered with the transferred materials from PI. For the composites with carbon fillers, on the contrary, the friction surfaces were remarkably covered with the transferred materials from composites, although the extent of coverage differed somewhat among the three types of composite. We also analyzed the friction surfaces of balls sliding against PI-10NH and PI-10NT using Raman spectroscopy. The Raman spectra of the center of the ball friction surface against PI-10NH and NH on PI-10NH virgin surface are shown in figure 13. The spectrum of the ball friction surface was similar to that of NH on the composite virgin surface, although the G and D peaks for the ball friction surface were fairly blunt compared with that for NH. Incidentally, the spectrum of NH on composite virgin surface almost coincided with that of original NH powders [2]. This fact clearly indicates that the transferred materials on the ball friction surface contained NH.

3.5. Discussion

The experimental results showed that both NH and NT have excellent wear reduction ability when used in PI-based composites, compared with Gr. This difference of wear property between the composite with NH or NT

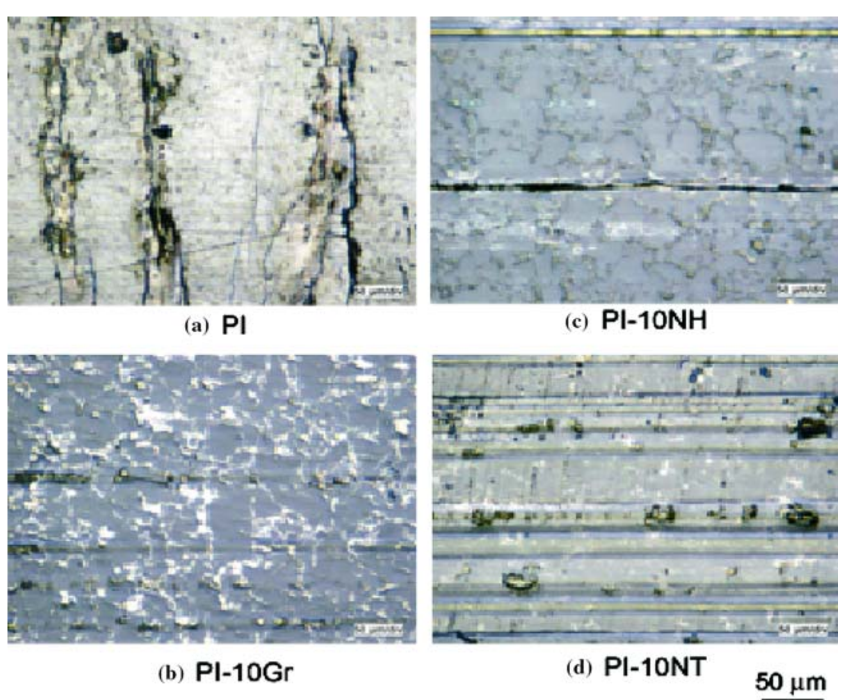

Figure 10. Friction surfaces on composites with different carbon fillers at the load of 25 N.

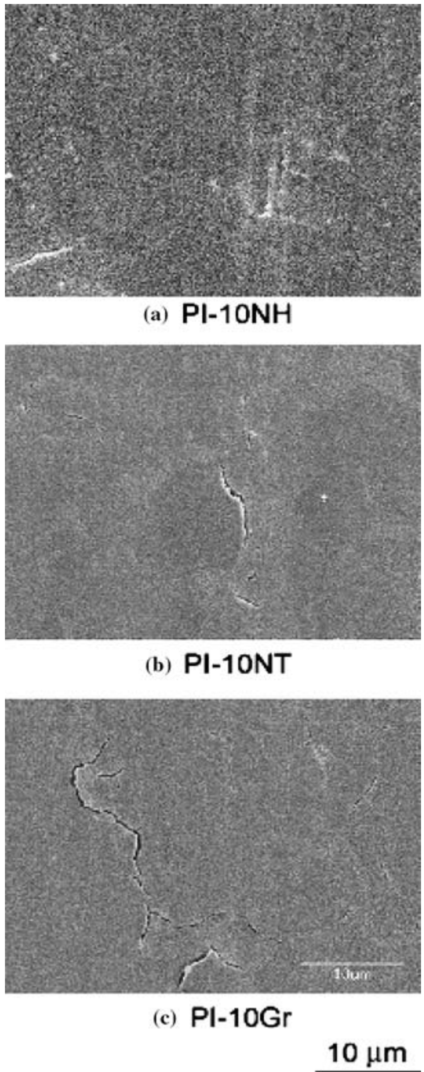

Figure 11. SEM micrographs of friction surfaces on composites with different carbon fillers at the load of 25 N.

and that with Gr is probably correlated with their different mechanical strengths; the hardness, an index of mechanical strength, of the composite with NH or NT was larger than that of Gr-containing composite, as shown in figure 4. Moreover, the wear reduction ability of NH was slightly better than that of NT; especially, the addition of only 5 wt% NH clearly decreased the composite wear compared with the addition of 5% NT. The microscope observations showed that the scratched lines on the friction surface of PI-NT composite were considerably clearer than those on the PI-NH composite surface (figure 10). From this observation, it is considered that the NT-containing wear fragments which detached from the composite surface abraded the composite surface more severely and hence promoted the composite wear. This reasoning is supported by the fact that NT is thin like conventional carbon fiber, which is known to abrade mating materials easily, whereas NH is spherical.

In our experiment, it was shown that NH and NT lower the friction coefficient of PI-based composites, similar to Gr. As mentioned in section 1, NH is an aggregate of horn-shaped sheath composed of single-wall graphene sheet, and NT also composes of graphene sheets, although there are multiple layers. It is well known that the interactive force between graphene sheets is caused by van der Waals force and is very weak, whereas carbon–carbon interactions in a graphene sheet are very strong [21]. The microscope observations and Raman analysis of the friction surface of the AISI 304 ball sliding against PI-NH composite showed that the transferred materials containing NH existed on the friction surface (figures 12 and 13), suggesting that the sliding between NH composed of graphene occurs at the interface of the composite and ball. In conclusion, the friction of composite containing NH was small as the interaction between graphene sheets is very weak. Furthermore, this low friction must contribute to the improvement of antiwear property of composite together with the increase of mechanical strength reflected to the hardness by the addition of NH. A similar consideration is applicable to the case of composite containing NT.

4. Conclusion

We fabricated polyimide (PI)-based composites containing single-wall carbon nanohorn aggregate (NH) using SPS process. For comparison, composites with carbon nanotube (NT) and traditional graphite (Gr) were also fabricated. Their friction and wear properties were evaluated using a reciprocating friction tester in air. The following results were obtained:

(1) NH drastically decreased the wear of PI-based composites; the specific wear rate of composite with NH of only 5 wt% was of the order of 10^{-8} mm^3/Nm, which was two orders of magnitude less than that of PI alone. The wear reduction ability of NT seemed to be slightly inferior to that of NH, although it was considerably better than that of Gr.
(2) NH and NT lowered the friction of composites. The friction coefficient of composite with 10 wt% NH was less than 0.25, although it was slightly higher than that of composite with 10 wt% Gr. There was no clear difference in friction reduction ability between NH and NT.
(3) The further addition of Gr to composites with NH or NT deteriorated the antiwear property of the composites, although the friction coefficient was reduced.
(4) The transferred materials existed on the friction surface of the mating ball sliding against composites with three types of carbon filler. These transferred materials seemed to correlate with the low friction and wear properties of composites.

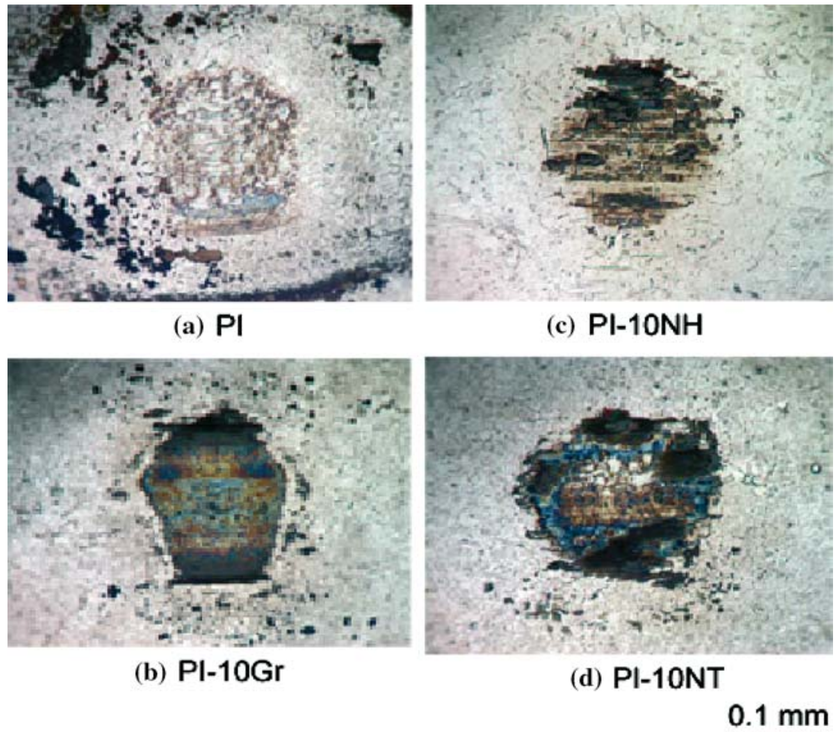

Figure 12. Friction surfaces of mating AISI 304 balls sliding against composites with different carbon fillers at a load of 25 N.

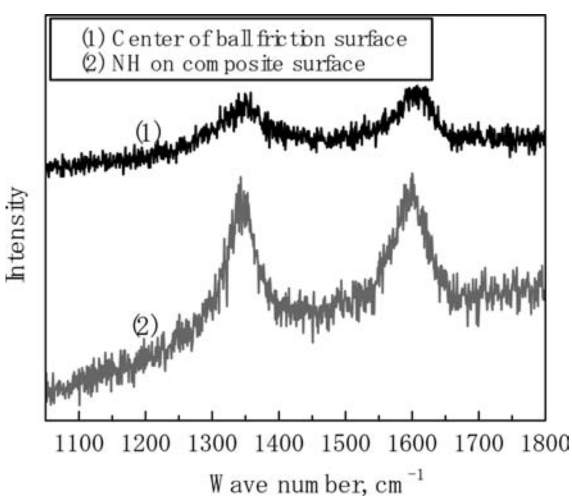

Figure 13. Raman spectra of friction surface of mating AISI 304 ball sliding against PI-10NH at a load of 25 N.

Acknowledgments

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